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EPR STUDY OF ELECTRON IRRADIATED LiF

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INTRODUCTION

It has been known for sometime that 100 - 1000 ev electron bombardment of an alkali halide substrate during or immediately prior to vapor deposition strongly influences epitaxy.[1,2,3,4,5] Workers in several laboratories have shown that the electron bombardment affects the orientation of the film and increases the number of nucleation sites. The efforts to understand the mechanism by which the alkali halide surface is altered have involved mass spectrographic measurements of the material released from the surface and LEED and Auger measurements of the surface structure.[6,7,8,9]

The bombardment causes the release to the vapor phase of alkali metal and halogen as neutrals, the halogen being more abundant, in the range from room temperature to 573 K. The LEED and Auger studies of Palmberg and Rhodin[9] suggest that the surface defects generated are mainly halogen ion vacancies and they therefore postulate that the additional nucleation sites formed are clusters of these vacancies. It was of interest to us to see whether surface F-centers might also be produced. Palmberg and Rhodin reported that coloration in KCl was obtained well below room temperature while Tokutaka et al report visible coloration in LiF and NaF at room temperature but not in KCl, NaCl and MgO. The detection technique we used was EPR, which might also be expected to detect the presence of free alkali metal if it exists in the proper state of subdivision. The preferential loss of halogen to the vapor might presuppose the retention of alkali metal on the surface.

EXPERIMENTAL

The material used in this study was melt grown Harshaw lithium fluoride ground in a mortar to a particle size range from 250 to 420 microns. The bombardment apparatus is shown schematically in Fig. 1. The salt was spread in a single layer on a one inch square gold plated pan connected to ground thru a microammeter. Gold plating was found to be necessary to prevent the liberation of oxygen from the oxide layer present on any other pan material. The salt was bombarded up to 4 hours with 300 volt electrons at a current level of 80 microamp/cm^2. The electron beam was pulsed, being on 25% of the time during a 15 second cycle. Pulsing was used to minimize heating and to permit possible surface charges to leak off. An unbaked ion pumped vacuum

system was used from which hydrocarbons were carefully excluded. The pressure during bombardment was in the range 10^{-8} to 10^{-7} torr. The concentration of oxygen and nitrogen in the ambient gas was reduced to a low value by backfilling with argon several times during the initial cryopumping of the system.

After bombardment, the pan was tipped by rotation of its support and the salt was collected in a 4 mm quartz EPR tube which was then sealed off. The EPR spectrum was obtained at X-band frequency. Spectra were recorded with the sample at room temperature and also at 77 K. Absolute intensities and "g" value determinations were obtained by comparison with a calibrated pitch sample using a dual cavity.

The EPR spectrum was found to be stable with time for at least a week. This is in contradistinction to the LEED patterns which were observed by Tokutaka et al[7] to reconstruct after a few hours at room temperature.

RESULTS AND DISCUSSION

The electron bombardment for a 4 hour period at 300 volts and 80 microamp/cm^2 with a 25%-on cycle produced a slight tan color and deposits which were black under the light microscope. The black deposit was found only on one surface of the crystallite - presumably that exposed to the electron beam.

The EPR signal obtained generally consisted of two components: a narrow line about 3.5 gauss wide lying on a broad line about 70 gauss wide (Fig. 2). The broad line was ascribed to the F-center[10,11] in LiF. It had a g value of 2.0017 and fitted a Gaussian line shape. It obeyed Curie magnetism on cooling to 77 K and it could be destroyed with UV light (λ = 2537 A). The hyperfine structure usually observed was not apparent for our polycrystalline samples because the hyperfine lines are angular dependent.

The narrow line was ascribed to lithium metal.[12,13] It had a g value of 2.00288 and fitted a Lorentzian line shape. If the F-center was removed by UV irradiation and the sample cooled to 77 K, the narrow line obeyed Pauli magnetism and the line width remained constant. This is consistent with the observation by Feher and Kip.[12] In addition, exposure to air eliminated the signal and converted the black deposit to the light reddish-brown color characteristic of Li_3N. The signal was symmetrical even at 77 K indicating that the lithium particle size was less than a micron in diameter.

As one would expect, minimal exposure to nitrogen or oxygen are required if the free metal is to be retained on the surface. In our system, backfilling with argon on pumpdown, long irradiation time and a gold plated pan gave successful results. Short irradiation times or

lower electron energies (~100 volts) yielded only the F band. It is presumed that the initial part of the bombardment period caused the desorption of surface impurities such as water and CO_2 so that short bombardment times or lower electron energies did not allow for the exposure of clean surface and the formation of lithium metal in the absence of reactive gases. A heated specimen holder which would allow for outgassing at high temperatures is required to explore the effect of electron energy and surface temperature. Lower electron energies are also needed to determine the depth to which F-center are formed. It is presumed that they lie within a few atom layers of the surface because the electron energy is too low to allow deep penetration. However, experiments at several energies lower than 300 volts are needed to clarify this point. The admission of CO_2 to form CO_2^- centers on the surface may also be useful to identify surface F-centers if their concentration is large enough to yield a detectable EPR peak. The CO_2^- radical ion has been observed[14] to form by the interaction of CO_2 with surface electron traps in MgO.

The number of electron spins detected was obtained by calibration with strong pitch. The number, 10^{14} per cm^2 of irradiated surface, corresponds to approximately one atom layer of lithium. The shape of the EPR peak and the observed black deposits lead us to conclude that the lithium exists as aggregates rather than as a uniformly dispersed monolayer. If we assume that the larger number of nucleation sites observed by Palmberg and Rhodin are in fact aggregates of lithium atoms, their size is of the order of several hundred atoms for a nucleation site density of 10^{12} cm^{-2} (estimated from their Figs. 4(a-1) and 5(b-2) of ref. 3). It is reasonable to expect that metal atom clusters of this type would be preferred over negative ion vacancies as crystallization nuclei for vapor deposited metal. The fact that the F-centers must be formed either on the surface or very close to it may explain the observation by the other investigators that they are observed in LiF and NaF but not in KCl and NaCl. Loss to the vapor phase of the neutral halogen and concommitant stabilization of the F-center would be much more favorable for the fluorine atom because of its small size.

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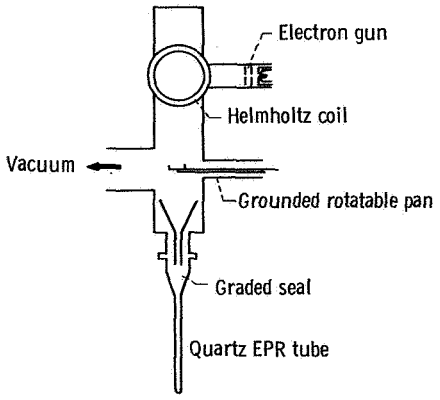

Figure 1. - Electron bombardment apparatus.

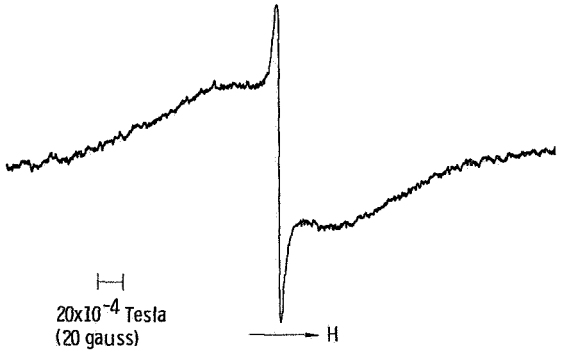

Figure 2. - EPR spectrum of electron irradiated LiF.